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TITLE: ACOUSTIC VELOCITY MEASUREMENTS ON FLUID METALS FROM TWO-FOLD COMPRESSIONS TO TWO-FOLD EXPANSIONS

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ACOUSTIC VELOCITY MEASUREMENTS ON FLUID METALS FROM TWO-FOLD COMPRESSIONS TO TWO-FOLD EXPANSIONS

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I. INTRODUCTION

Fluid metals around normal density can be thought of as low temperature non-ideal plasmas. They are plasmas in that the Coulomb interactions among the constituent particles are important in determining thermodynamic and transport properties. They are low temperature in that even up to 1 eV the temperature is less than or comparable to the average interionic electrostatic energy. The resulting high Γ's ($\Gamma = Z^2e^2/\langle r\rangle kT$) cause the pair distribution function to look more like that of a normal liquid than that of an ideal gas. For the present studies $\Gamma \sim 10\text{-}100\ Z^2$, where Z is the effective charge of the ions. The real metallic systems have several important differences from idealizations such as the one component plasma model. For example, since the mean distance between electrons, r_s, varies between 2 and 3 in atomic units with temperatures between 0.1 and 1 eV, the electron gas is degenerate, but polarizable. Therefore, unless the electron screening is well known, the effective Coulomb interaction between ions cannot be specified. Furthermore, according to the model of Ashcroft and Lekner,[1] the packing fraction along the liquidus remains roughly constant at 0.46. As a result the excluded volume of the ions probably cannot be ignored anywhere over the density range from two-fold compressed to four-fold expanded. These complexities make realistic modeling of dense fluid metals very difficult in practice.

Over the past several decades, we have developed techniques for accurate thermodynamic and transport measurements over a wide range of densities and temperatures. The two regions we shall concentrate on here are shock compression and heating to 1 eV and two-fold density increases, and isobaric expansion to 1 eV and four-fold density decreases. These experimental capabilities can now produce metal samples in stable, equilibrium states, defined to 1-2% in thermodynamic parameters, for times long enough to perform other experiments.

There are several reasons for choosing the acoustic velocity as a parameter to measure for dense fluid metals. First, the acoustic velocity is directly related to the adiabatic bulk modulus, a derivative of the equation of state surface in P,V,E space. Since the equation of state surface may be subtly affected by changes in interparticle potential, measurements of the derivative will be much more sensitive to these changes. For example, there is growing evidence that at least some of the conduction electrons are localized in fluid mercury as the density decreases below 9 gm/cc.[2] Since screening by the degenerate electron gas is accomplished by electrons near the Fermi surface, changes due to localization in the density of states at the Fermi Surface will certainly change the effective interparticle potential. There is indication that this effect can be seen in the acoustic velocity.[3]

Another reason for interest in acoustic velocities is that, when combined with accurate data along shock compression or isobaric expansion paths on the equation of state surface, these measurements allow a purely experimental determination of most of the important thermodynamic quantities. These include the heat capacity at constant volume, C_V, the isothermal bulk modulus, B_T, and Grüneisen's gamma, γ_G. The latter two quantities can be thought of roughly as the orthogonal derivatives of the P,V,T equation of state surface in that

$$B_T = -V \left.\frac{\partial P}{\partial V}\right)_T \quad ,$$

and (1)

$$\gamma_G = \frac{V}{C_V} \left.\frac{\partial P}{\partial T}\right)_V \quad .$$

In the following sections we will outline the methods of making acoustic velocity measurements on samples which are destroyed in time scales of milliseconds or less, the analytical techniques for calculating the thermodynamic quantities of interest, and new results indicating a linear relationship of acoustic velocity with density over a very large density range.

II. SHOCK COMPRESSION

Shock compression is one way of obtaining fluid metals at high temperature and density and in well defined thermodynamic states. The irreversible nature of shock compression results in large entropy or temperature increases, so that for sufficiently strong shocks the compressed material will be molten. The thermodynamic state is determined by the Hugoniot relations, which are nothing more than statements of conservation of mass, momentum, and energy across the shock front.[4] One complexity often encountered for solids is avoided when the shocked material is molten. Since the momentum conservation condition gives a Hugoniot equation referring to the longitudinal stress (i.e., in the direction of shock propagation), the stress tensor in the shocked solid may be undetermined. In the solid, longitudinal and transverse stresses may be different. However, if the shock melts the sample, the liquid cannot support significant deviatoric stresses, so the longitudinal and tangential stresses are identical. For this case the pressure is well defined.

The question of equilibrium often arises in shock wave physics. How does one know that the P,V,E point determined by dynamical measurements in a shock wave experiment determines a point on the equilibrium equation of state surface? In answer to that, we have a wealth of empirical evidence that dynamic and static high pressure data normally agree to within experimental uncertainties.[5] Furthermore, molecular dynamics calculations for monatomic systems, such as metals, indicate a very rapid equilibration of the translational degrees of freedom following an abrupt departure from equilibrium.[6] For these reasons we consider that the thermodynamic state behind a shock is both well defined and in equilibrium. We have developed techniques for measuring acoustic velocity in shock compressed materials primarily to determine high pressure melting points. If the compressed material is solid, this velocity is the longitudinal elastic wave velocity, while, if the material is partially molten, the highest velocity acoustic disturbance travels with the bulk wave velocity.[7] Since these velocities typically differ by 20–30%, it is easy to determine where the Hugoniot curve crosses the solidus.[8]

The basis for acoustic velocity measurements in shock melted metals is the use of a short shock, as illustrated in Fig. 1. When a thin plate hits a target, shocks move forward (to the right on Fig. 1) from the impact surface into the target and backward in the plate. When the shock reaches the free rear surface of the plate, the zero pressure boundary condition requires that a rarefaction wave propagates forward in the direction of the shock in the target. This situation corresponds to t = 0 in Fig. 1. The rarefaction wave is dispersive since the leading edge is moving into hot compressed material, in which the acoustic velocity normally exceeds the original shock velocity, while the trailing edge of the rarefaction is moving into decompressed material. When the rarefaction overtakes the shock wave the peak shock pressure decreases, as does the shock velocity. Previous attempts to measure the overtake by observing the decrease in shock velocity have often been ambiguous because the measured wave velocity scales roughly as $P^{1/2}$. In this case small changes in peak pressure result in even smaller changes in wave velocity.

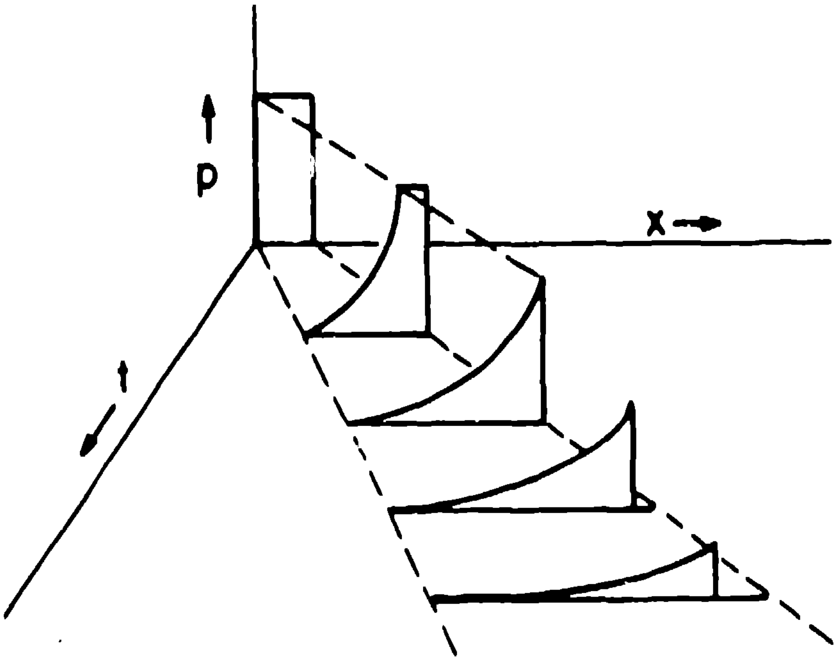

Figure 1. Evolution of a short shock. At t = 0 the release from a free surface begins to overtake the shock. When overtake occurs the peak pressure and shock velocity decrease.

The improvement we have introduced, which allows us to measure the acoustic velocity in hot materials at very high pressure, involves measuring the thermal radiation from the shock front in a transparent medium.[9] Since the thermal radiation intensity varies as a high power of the temperature at the shock front, or equivalently the shock pressure, small decreases in peak pressure result in much larger fractional decreases in detected light intensity. By choosing a transparent medium, the optical analyzer, in which the shock front is opaque, we can assure that we are measuring the leading edge of the shock wave structure. By varying the metal target thickness through which the shock wave structure must pass before entering the optical analyzer we can make measurements which allow us to extrapolate to a target thickness for which the rarefaction overtakes the shock at the target-optical-analyzer interface. This experimental technique eliminates the need of complex hydrodynamic calculations to account for perturbations due to waves reflecting from the metal-optical-analyzer interface.

The calculations required to obtain the acoustic velocity from the measured time for a release to overtake the shock have been presented in detail elsewhere.[10] Since the acoustic velocity in a fluid determines the slope of an isentrope centered on the shock state, and the P-V relation determined by the Hugoniot equations (referred to as the Hugoniot) determines the slope of a different, stiffer curve on the equation of state surface, by differencing them one can obtain an expression for the Grüneisen parameter:

$$\gamma_G = V \left.\frac{\partial P}{\partial E}\right)_V$$

$$= V \, \frac{\partial P/\partial V)_S - \partial P/\partial V)_H}{\partial E/\partial V)_S - \partial P/\partial V)_H} \, , \qquad (2)$$

where the subscript S refers to the isentropic derivatives, while the subscript H refers to derivatives along the Hugoniot. If one also measures or calculates the temperature along the Hugoniot, the constant volume heat capacity can be calculated from[11]

$$C_V = \frac{(\partial E/\partial V)_H + P}{(\partial T/\partial V)_H + (\rho\gamma)T} \; . \qquad (3)$$

The isothermal bulk modulus is then derived from

$$B_T = B_S - \alpha B_T \gamma T$$

$$= B_S - (\rho\gamma)^2 (C_V/\rho) T \; . \qquad (4)$$

These equations have been used to obtain all the useful thermodynamic data for fluid CsI, for example, up to 1.5 Mbar and 10,000 K.[12]

Some of the results we have obtained for acoustic velocity in shock compressed metals are shown in Fig. 2. In the case of iron we found evidence of a solid-solid transition at a shock pressure of 2 Mbar and melting at 2.5 Mbar. The data along the extension of the bulk sound velocity curve (C_B) are for the liquid phase. In the case of tantalum we observed only the melting transition. In both of these cases the acoustic velocity is a linear function of density along the Hugoniot in the liquid phase.

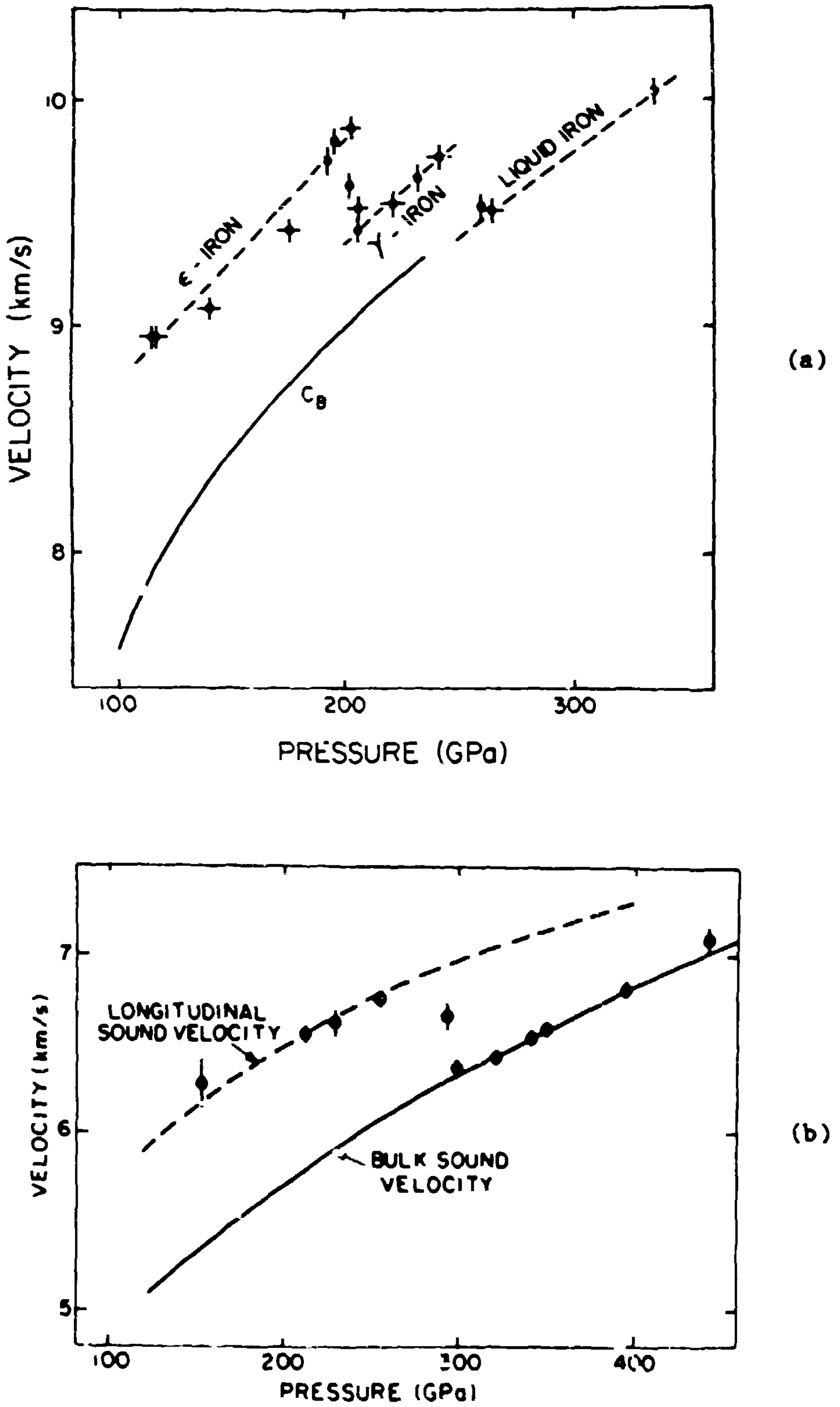

Figure 2. Rarefaction wave velocity as a function of shock pressure. (a) Iron (Ref. 13); (b) tantalum (Ref. 14). C_B refers to the bulk sound velocity.

III. ISOBARIC EXPANSION

The isobaric expansion experiment has been developed over the past decade to provide stable, equilibrium liquid metal samples up to four-fold expansion and 10,000 K.[15] The experiment consists of a wire electrically heated in an inert gas filled pressure vessel. The roughly square electrical pulse, with 5 μsec rise and fall times and 30–100 μs duration is chosen so that an approximately 1-mm-diameter wire is heated quickly enough to avoid hydrodynamic instabilities, such as the capillary instability. On the other hand the heating pulse is slow enough so extra heating of the surface through the skin effect is avoided, and the pressure throughout the sample is nearly constant during the expansion. Enthalpy is calculated as the time integral of the current times the voltage, with the current and the voltage measured during the heating pulse by a four probe method. Temperature is determined by multicolor optical pyrometry of the wire surface, so the inert gas prevents chemical reaction giving non-thermal radiation as well as providing the pressure medium. By increasing the pressure to supercritical, stable expansions can be obtained to roughly the critical density (~4-fold expansion).

With this capability we have demonstrated that one can obtain good pressure, density, enthalpy, and resistivity data along an isobaric expansion curve. With the addition of pyrometric temperature determinations, the constant pressure heat capacity is also available.[16] For dense metals, such as tantalum and lead, the liquid column remains stable for tens of microseconds after the current is turned off, even at temperatures above 8000 K.

The basis for acoustic velocity measurements in this thermodynamic regime is a laser induced stress wave. After the current pulse has been stopped, but before the liquid column falls apart, we irradiate one side of the sample with a 0.1-0.5 J, 25 ns, pulsed ruby laser propagating radially. With a focal spot of 100 μ diameter we can generate a 10 kbar stress wave, the velocity of which rapidly decays to the sonic velocity. This wave propagates across a diameter of the wire and emerges at the opposite side, causing a compression wave in the gas. With Schlieren photography, we can photograph this wave in the gas and determine when it breaks out of the sample. The sound velocity is then calculated from the time interval and the sample diameter.[17]

Data from many experiments on lead and tantalum are shown in Fig. 3. We have chosen density as the independent variable to show the linear dependence of sound velocity on density, over a factor of two expansion in the lead data. Several pressures are represented in Fig. 3a, and, at least in the low density data we can obtain a rough upper limit on the intrinsic temperature dependence of the sound velocity. Since at a density of 5-6 gm/cc the temperature spread between 1 and 3 kbar isobars is greater than 500 K and the accuracy of the sound velocity data is better than 4%, the independence of sound velocity on pressure gives

$$\frac{\partial c}{\partial \ln T} < 0.3 \text{ km/sec} \quad .$$

On the other hand, from Fig. 3a we can determine that

$$\frac{\partial c}{\partial \ln \rho} \sim 1 \text{ km/sec} \quad .$$

Therefore the intrinsic temperature dependence at large expansions appears to be much weaker than the density dependence.

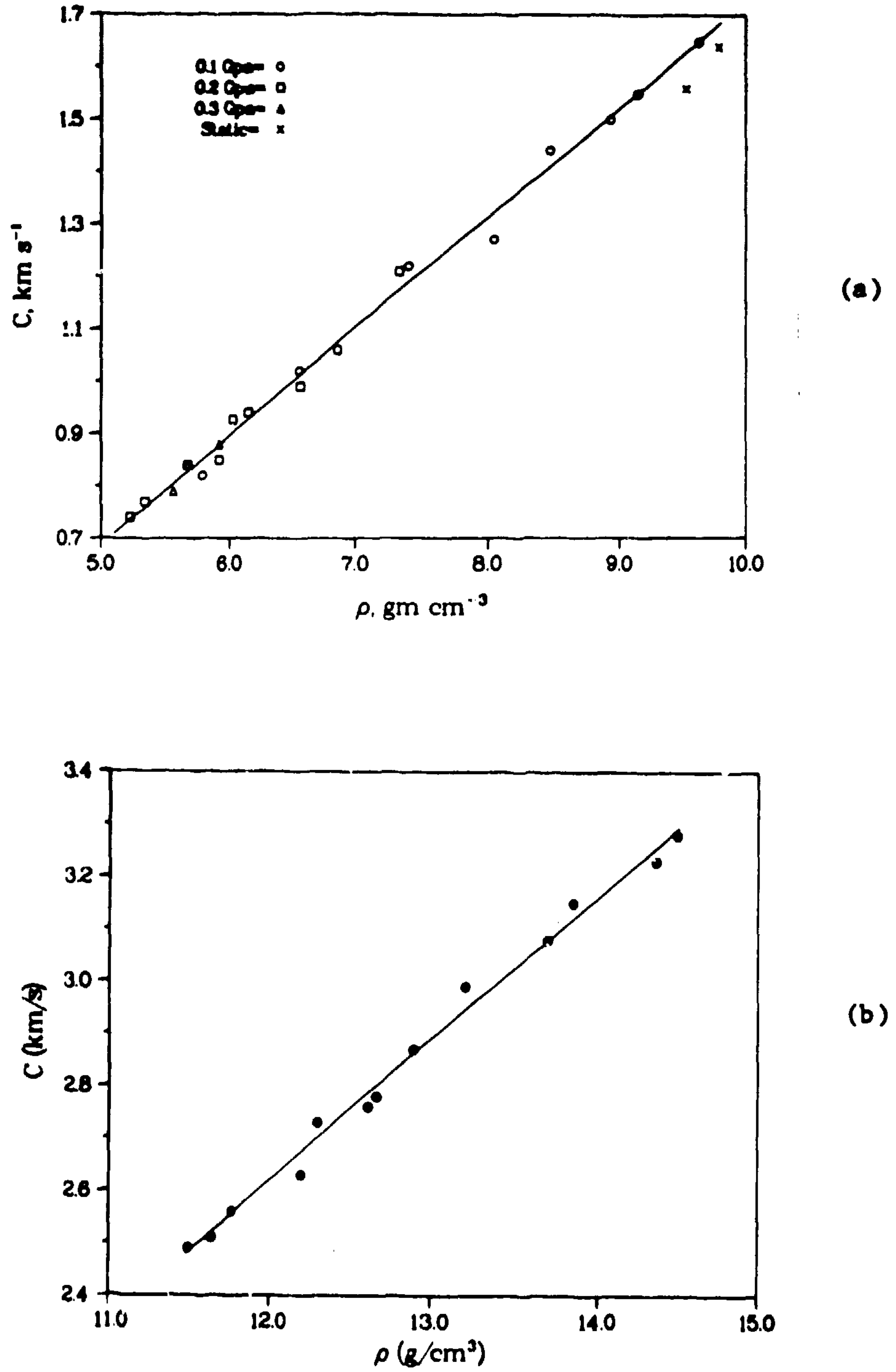

Figure 3. Acoustic velocity in heated, expanded liquid metals: (a) lead (Ref. 13); (b) tantalum (Ref.19).

The linearity of the precent data with density is consistent with other measurements of sound velocity in fluid metals over much narrower density ranges.[20] Typically C is reported as linear in T at constant pressure.[21] However, the apparent temperature dependence is probably implicit through thermal expansion.

Given the previously obtained thermodynamic properties and the sound velocity, we can use the relations

$$C_P = C_V + \alpha^2 V T B_T \quad , \tag{5}$$

with α the thermal expansion coefficient, and

$$c^2 = V B_T \, C_P / C_V \quad , \tag{6}$$

to determine experimentally both C_V and B_T. Also, we can express Grüneisen's gamma as

$$\gamma_G = \left(\frac{\partial V}{\partial H}\right)_P c^2 \quad , \tag{7}$$

so the isobaric expansion data and sound velocity completely determine the derivatives of the equation of state surface.

IV. BIRCH'S LAW

With a linear density dependence of sound velocity both in compression and expansion for fluid metals, it is natural to plot both sets of data together. The only fluid metal for which we have data both in shock compression and isobaric expansion is tantalum, and this is shown along with other available data in Fig. 4. These data show that for tantalum the same linear relation fits both sets of data from 10 to 30 gm/cc. The lead data from isobaric expansion is extrapolated to high density by using the common assumptions for shocks in condensed media: shock velocity linear in material velocity and $\rho\gamma_G$ constant. The reasonable linearity of sound velocity vs density is again to be seen. The iron and aluminum shock data are augmented by one-atmosphere data on molten liquids.[22,23] The one material which appears to fall outside the uniform collection of data is lanthanum, for which the slope appears steep. However, we know that the acoustic velocity of this metal is affected by changes in the electronic band structure in the density range shown here.[10] The other systematic feature of Fig. 4 is that the slope of the linear relations is monotonically decreasing in atomic mass.

This kind of plot has been presented first by Birch in an attempt to derive the average atomic number of materials deep in the earth from seismic velocities. Birch started by measuring elastic wave velocities in rocks to 10 kbar, representing a density change of less than 10%.[24] He later included shock compression data, from which isentropic moduli were calculated or the shock wave velocity was used directly, to establish Birch's Law: for isostructural materials the wave velocity decreases as the square root of the mean atomic mass, while for a given material the wave velocity increases linearly with density.[25] Since the original work, several people have tried to explain this linear relation as an approximation to more general solid state models over a limited density range.[26] The present data show an apparent linearity over a much wider density range than has been previously considered.

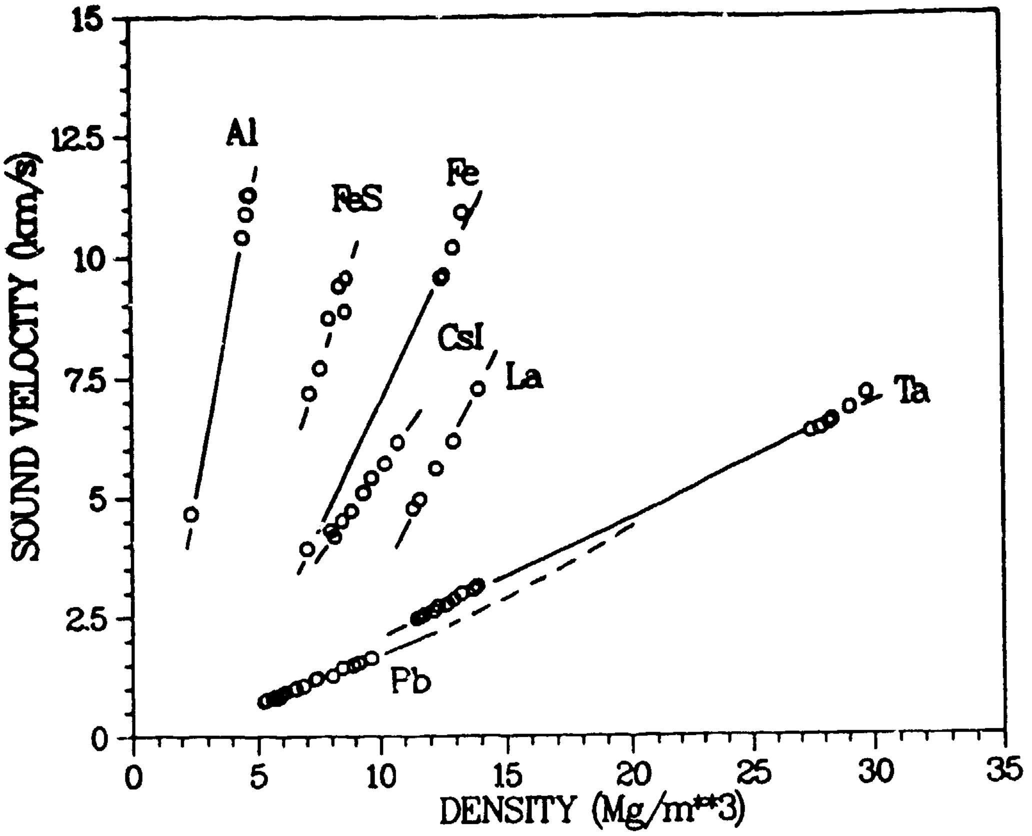

Figure 4. Density dependence of sound velocity for liquid metals

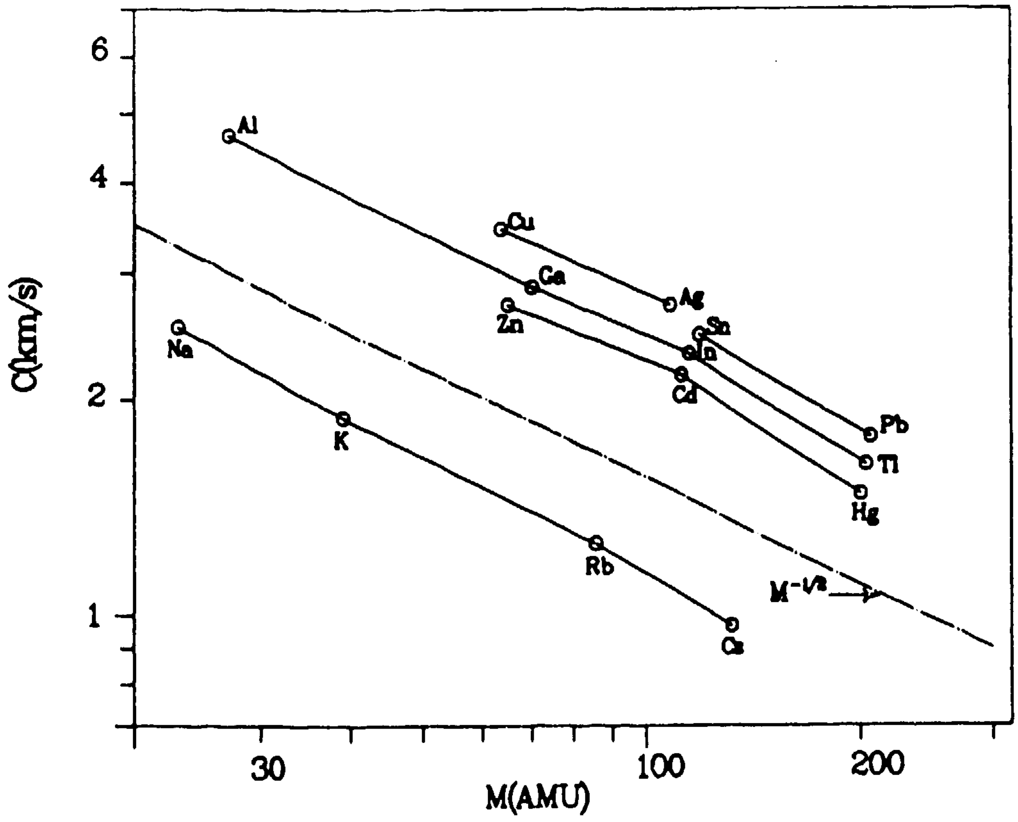

Figure 5. Acoustic velocity of liquid metals as a function of at
mass. The thermodynamic state is the 1 atmosphere mel
point in all cases (Ref. 23).

The first half of Birch's law is that isostructural materials should have a wave velocity which scales inversely with the square root of the mean atomic weight. In Fig. 5 we show that this scaling works very well for liquid metals at the 1 atmosphere liquidus. According to the work of Ashcroft and Lekner,[1] all metals at this point have roughly the same packing fraction, so the structures are closely similar. The metals group naturally according to column in the periodic table so the offsets must be determined by a combination of the valence, or core charge, and the core electronic structure. These figures show that we have rediscovered Birch's law for fluid metals.

V. DISCUSSION

A starting point for understanding acoustic velocity in fluid metals is to consider the disturbance as an ion plasma wave. The unscreened ion plasma wave frequency is given by

$$\Omega_p^2 = \frac{4\pi n(Ze)^2}{M} , \tag{8}$$

where n is the ion density, Z is the ionic charge and M is the ionic mass. Screening by a gas of free electrons introduces a q dependence through the dielectric function which results in a dispersion relation

$$\omega_p = cq , \tag{9}$$

where

$$c = \left(\frac{nZ^2}{MN(E_F)}\right)^{1/2} , \tag{10}$$

and $N(E_F)$ is the density of states at the Fermi surface. $N(E_F)$ scales as $n^{1/3}$, so c, although it has the proper dependence on ionic mass and temperature, should vary as the cube root of the density in this model, and not linear with density. This model, developed by Bohm and Staver, also fails to give proper quantitative values to within a factor of two except for the alkali metals.[23]

By putting terms which are functions of Γ in the free energy of the system, one gets no closer to the experimental data. If the Helmholz free energy is a function of Γ, as in the one-component plasma model,[27] then

$$\begin{aligned} B_T &= \rho \left.\frac{\partial P}{\partial \rho}\right)_T \\ &= \rho \frac{\partial}{\partial \rho} \left[\rho^2 \left(\frac{\partial F}{\partial \rho}\right)_T\right]_T \\ &= \frac{1}{9} \frac{\rho^{5/3}}{(kT)^2} \left(\frac{\partial^2 F}{\partial \Gamma^2}\right)_T . \end{aligned} \tag{11}$$

Ignoring the distinction between adiabatic and isothermal moduli, this expression suggests a stronger temperature than density dependence for the sound velocity.

Two models which do reproduce the experimental results are variations on the van der Waals equation of state. They are the hard sphere van der Waals theory of Young and Alder[28] and a more realistic soft sphere version.[29] Both of these models are of the form

$$P = \frac{NkT}{V}\left[1 + A(\rho,T)\right] - B(\rho) \quad ,$$

and (12)

$$E = E_0 + NkT\left[\frac{3}{2} + C(\rho,T)\right] - D(\rho) \quad ,$$

where the functions A, B, C, and D are determined by fits to Monte Carlo simulations of systems with hard sphere or soft sphere potentials. The various parameters, such as hard sphere radius, or the power of the soft sphere potential, can be fit consistently to the data for fluid metals, including the linear density dependence of the sound velocity. Two differences between these models and the Bohm-Staver or one component plasma model are that the potentials are stiffer and that the non-zero core size is explicitly included. It is not clear which of these differences is most important in correcting the point charge models. The van der Waals models are semi-empirical, however. The more fundamental theories, such as those developed by Ashcroft and Langreth[30] have not yet been applied to the density dependence of the bulk modulus.

Recent measurements by Shaw and Caldwell on fluid alkali metals up to 7 kbar and 450 K have given similar results to ours, although over a much more limited thermodynamic range.[21] They find a weak temperature dependence and a roughly linear density dependence of acoustic velocity. However, their data is presented in terms of "experimentalist variables" - pressure and temperature - instead of density and temperature. Until the inversion is done the accuracy of Birch's law cannot be confirmed.

We have shown that with current experimental techniques thermodynamic quantities can be measured accurately for fluid metals over a four or five-fold density range up to temperatures of 10,000 K. The result we have presented here is that the acoustic velocity in these systems is apparently relatively insensitive to temperature and linear in density over a very wide thermodynamic range. We believe that the ionic core properties are important in determining this result both through their finite size and in the stiffness of the potential relative to a point change system. However, the question still remains: Why is Birch's law so good?

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